Proceedings of ISSMS - 2004

International Symposium on Smart Materials & Systems Dec.15th - 17th, 2004

Velammal Engineering College
'Velammal Nagar', Ambattur Redhills Road,
Surapet, Chennai - 600 066.

& ISSS

Effect of different processing parameters on preparation of doped soft PZT powders and fabrication of multilayered stacks

B.Sahoo, V.A. Jaleel and P.K. Panda*

Materials Science Division
National Aerospace Laboratories
Bangalore- 560 017

Abstract

The use of piezoelectric materials for actuator applications has been steadily increasing in recent years. For better performance, actuators should be fabricated from PZT materials of high d_{33} values and from large number of thin strips. PZT compositions near morphotropic phase boundary (MPB) with donor dopants are generally selected to get high piezo properties. In view of the above, we have studied the compositions $Pb_{1-x} M_x (Zr_{0.53}Ti_{0.47}) O_3$, where M = La^{3+} (0-8 mole %), Nd^{3+} (0-6 mole %), Sr^{2+} (0-3 mole %) and their combinations. The powders were prepared by wet chemical method using chlorides and nitrates as precursors. The powders were calcined in the temperature range of 650-900°C, pelletized and sintered in the temperature range of 1050-1250°C. The effect of different dopants as well as the effect of calcination and sintering temperatures on piezo- properties was studied. The sintered pellets were electroded, poled and were characterized for piezoelectric charge coefficient (d_{33}), capacitance and loss factor with an operating frequency of 100Hz at room temperature. The dielectric constants of the samples were calculated from the measured capacitance values. From the above study, the maximum d_{33} value of 234 pC/N for 2 mole% La^{3+}, 260 pC/N for 2 mole% Nd^{3+} and 202 pC/N for 1 mole% Sr^{2+} were obtained. Similarly, in case of combined dopants, a combination of 1 mole% Nd^{3+} and 1 mole% Sr^{2+} produced a maximum d_{33} value of 313 pC/N. PZT powders were uniaxially pressed in the form of rectangular blocks, sintered in a lead rich atmosphere, cut into thin strips of equal sizes and were leveled, polished, electroded and poled in a dc field of 2KV/mm. PZT stacks were fabricated by stacking the strips by layering them ensuring the desired electrical connectivity. The static displacements of the stacks were measured by applying a dc voltage and were recorded by a strain gauge of 1μm resolution and the % free strain was calculated. The maximum displacement of 20μm was recorded at an applied voltage of 650V. The effective inverse piezoelectric coefficient (d_{33}) of the stacks in the direction of the applied field were calculated by using the relation $d_{33}=\Delta t/(nV)$, where "Δt" is the displacement, "V" is the applied voltage and "n" is the number of the active piezoelectric layers in the actuator. The free strain was 0.1% and the inverse d_{33} coefficient was 1150×10^{-12} m/V respectively at 650V. Further studies on effect of thickness of PZT layers as well as number of layers on displacement are under progress.

* Corresponding author, E mail- pkpanda@css.cmmacs.ernet.in

Introduction

Lead Zirconate Titanate (PZT) is an important material used for "smart" applications i.e. for both sensing as well as for actuating purpose. It is a solid solution of lead zirconate ($PbZrO_3$) and lead titanate ($PbTiO_3$). It possess excellent piezoelectric properties such as high piezo-electric charge constant (d_{33}), high coupling coefficient, high dielectric constant etc. and is used as actuators and sensors, as sonar transducers, as accelerometers, in inkjet printers etc. The highest piezoelectric coupling coefficients as well as maximum permitivity are obtained for compositions near morphotropic phase boundary (MPB) which fall in between the tetragonal and rhombohedral phases [1-3]. The properties of PZTs are further enhanced by addition of suitable dopants. The powders are generally prepared by various methods like mixed oxide, sol-gel, co-precipitation, spray drying, hydrothermal synthesis etc. Synthesis of PZT powders by conventional "mixed oxide" route requires a fairly high sintering temperature, which causes significant loss of lead oxide [4]. Other disadvantages of this process are compositional inhomogeneity, impurity pickup during milling and large particle size of the powder. All these factors degrade the properties. Therefore, several chemical methods are followed for preparation of PZT powders, which generate very fine, stoichiometric, homogeneous powders [5-9]. Among these methods, wet-chemical, co-precipitation [9,10] and sol-gel [11] techniques are most popular.

The present study is basically focused on the preparation of PZT powders by wet-chemical method with addition of soft variety "A" site dopants such as La^{3+} (0-8 mole %), Nd^{3+} (0-6 mole %), Sr^{2+} (0-3 mole %). In this method, PZT powders were prepared mainly from inorganic precursors such as nitrates, chlorides etc. The piezo properties of the compositions were extensively studied by varying dopant concentration. Some multi-layered stacks (25 layers) were also fabricated by using the in house prepared PZT powder. The displacement, % free strain and effective d_{33} values of the multi- layered stacks were measured.

Experimental

Preparation of PZT powders by wet-chemical method

Water-soluble inorganic salts such as nitrates and chlorides were used as starting raw materials. The salts were dissolved in de-ionised water and filtered to remove the suspended impurities. Clear solutions of lead, zirconium and titanium salts in stoichiometric amount including dopant salt solutions were intimately mixed to get a homogeneous and clear solution. This combined solution containing 3% excess lead were converted into mixed hydroxides by slowly raising the pH, adding ammonia solution. The mixed hydroxide was thoroughly washed, filtered and dried at 110-120°C over night. The dried powder was calcined in the temperature range of 750-900°C for 1-4 hours. After calcination, the powders were de-agglomerated and PZT phase formation was confirmed by XRD analysis (M/s. Phillips, Holand).

The calcined powders were then granulated, and uniaxially pressed into pellets. This pellets were sintered in the temperature range of 1050-1250°C for 2 hours in a closed crucible in a lead rich atmosphere. The sintered samples were characterized for lead loss, sintered density, phase analysis and microstructure. For evaluation of piezo properties sintered discs were leveled, polished, electroded and poled in a dc field of 2KV/mm. The d_{33} strain coefficient was measured using a piezo-meter (model PM-35, M/s.Take control, UK).

Result and Discussion

The properties of lanthanum, neodymium and strontium doped PZTs are given below in table-1, table-2 and table-3 respectively.

Table-1: Properties of lanthanum doped PZTs

Conc. of Lanthanum (mole)	Weight Loss (%)	Sintered Density(%Th)	d_{33} (pC/N)	Dielectric constant (K)	Tanδ
0.00	1.8	93.5	114	367	0.0026
0.02	1.22	95.5	234	497	0.0186
0.04	0.86	96.5	223	546	0.0281
0.08	0.48	94.6	208	600	0.0486

Table-2: Properties of neodymium doped PZTs,

Conc.of neodymium (mole)	Weight Loss (%)	Sintered Density(%Th)	d_{33} (pC/N)	Dielectric constant (K)	Tanδ
0.00	1.8	93.5	114	367	0.0026
0.02	1.6	96.6	260	924	0.0176
0.04	0.41	97.3	229	975	0.0187
0.06	0.16	97.8	215	1023	0.0195

Table-3: Properties of strontium doped PZTs

Conc.of Strontium (mole)	Weight Loss (%)	Sintered Density(%Th)	d_{33} (pC/N)	Dielectric constant (K)	Tanδ
0	1.8	93.5	114	367	0.0026
0.01	1.62	96.0	202	473	0.0183
0.02	1.35	94.7	180	490	0.0190
0.03	1.04	94.0	164	517	0.0185

Table-4: Properties of mixed dopant PZT

Conc.of dopants (mole)	Weight Loss (%)	Sintered Density(%Th)	d_{33} (pC/N)	Dielectric constant (K)	Tanδ
La(0.01)&Nd (0.01)	1.27	96.5	246	980	0.0235
Nd (0.01) & Sr 0.01)	1.7	95.6	313	915	0.0213
La(0.01)&Sr (0.01)	1.8	95	294	820	0.024

The % weight loss of lanthanum doped samples were found to be within 2%. The value slightly decreases with increase in dopant concentration. This may be due to the formation of PbO liquid phase at the grain boundaries which is not suppose to leave the samples. The same trend is also observed for "neodymium" and "strontium" doped samples. The sintered density for all the samples were found to be in between 93-98 % of theoretical value.

Piezoelectric and dielectric properties

The variation of longitudinal piezoelectric coefficient (d_{33}) with respect to dopant concentrations is presented in **Fig.1.** The d_{33} value for undoped sample was found to be 114 pC/N, which is enhanced by the addition of dopants. This is due to the soft nature of dopants which facilitates the domainwall motion and enhances easy reorientation of dipoles in the presence of a d.c field. There is a sharp increase in d_{33} value at 2.0 mole % of lanthanum and it drops with increase in dopant concentration. In case of neodymium doped PZT it is observed that the d_{33} is maximum (260 pC/N) at 2 mole% Nd^{3+}. Similarly the d_{33} value of the strontium doped PZT sample is maximum (202 pC/N) at 1 mole% of strontium.

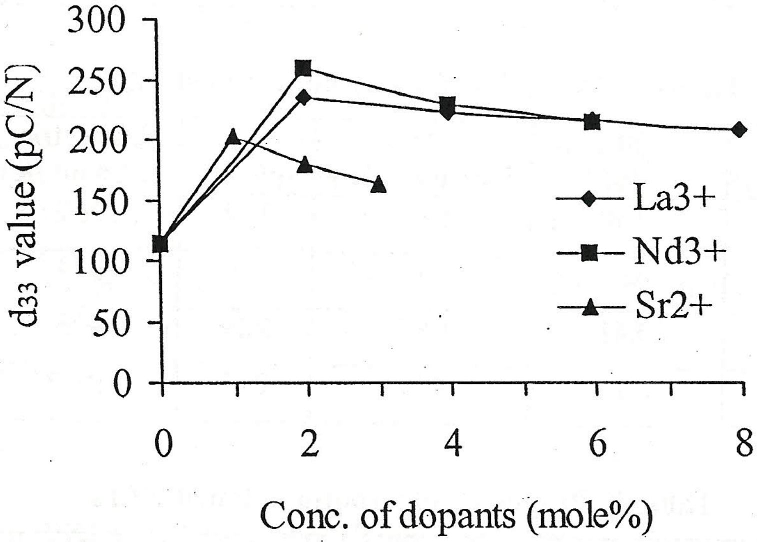

Fig.1: d_{33} values as a function of dopant concentration

The dielectric constant of the samples were measured from the respective capacitance values by using the following formula,

$$\text{Dielectric constant (K)} = \frac{C \times t}{\varepsilon_o \times A}$$

Where C= Capacitance of the sample
t= thickness of the sample
ε_o= permitivity of the free space (8.854×10^{-12} F/m)
A= electroded area of the sample

The variation of dielectric constant of the samples with different dopant concentration is shown in **fig.2**. It is observed that the dielectric constant of the poled samples gradually increase with increase in lanthanum content. The same trend is also observed in case of neodymium and strontium doped samples. This may be due to increase in grain size of the samples with increase in dopant concentration [12].

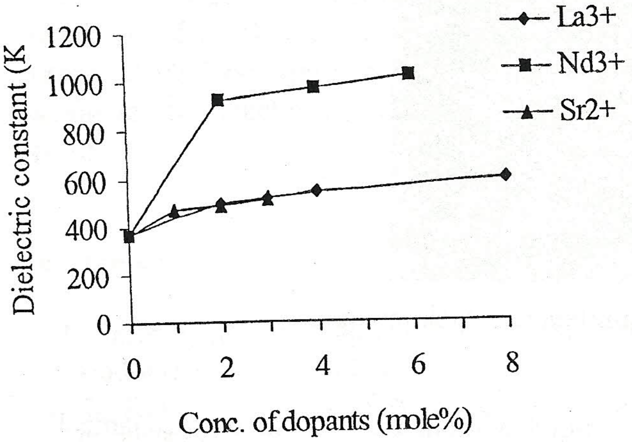

Fig.2: Dielectric constant as a function of dopant concentration

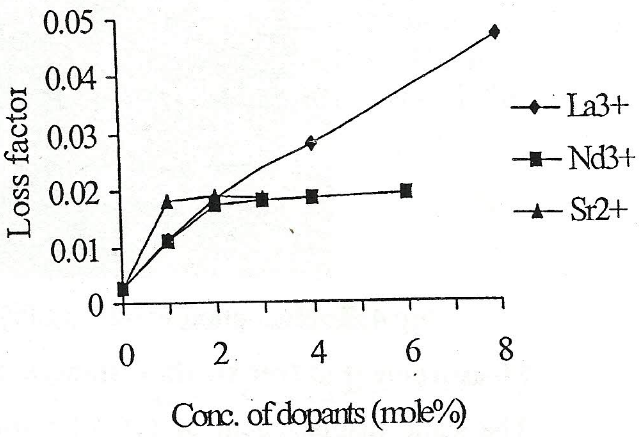

Fig.3: Loss factor as a function of dopant concentration

Loss Factor

Variation of loss factor as a function of lanthanum, neodymium and strontium content is shown in **fig.3**. The loss factor of undoped sample is very low (0.0026) as compared to doped samples. It slightly increases with increase in lanthanum concentration. The same trend holds good for Neodymium and Strontium doped samples.

Fabrication of Multi layered Stack

Multi-layered (25 layer) stacks were fabricated by using in house prepared PZT powder. The powders were consolidated into rectangular blocks of dimension 26x21x14 mm^3. The green blocks were sintered in a lead rich atmosphere to get good sintered bodies. The sintered blocks were cut into thin strips (18x 12x0.75 mm^3). Finally the strips were leveled, polished, electroded using silver paste and poled in a dc field. Strips having almost equal d_{33} values were selected for fabrication of multi layered stack. The internal electrodes were designed in such a way so that they do not extend to the edge of the components, except for the end terminals. Layering / stacking of the strips was done carefully so that alternate layers were connected to the same terminals. Typical figure of multi-layered stacks of 25 layers is shown below in **Fig.4**.

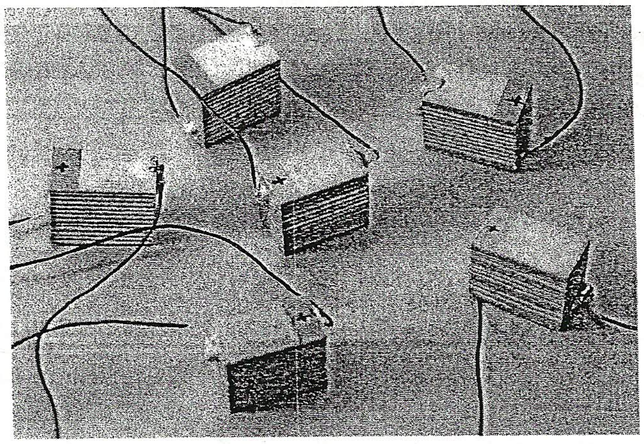

Fig.4. Typical photographs of PZT multilayered stack/ actuator.

Measurement of free strain/displacement

The static displacement of actuartor was measured without application of mechanical load by applying a dc voltage of 0-650V. The displacement generated was measured with a displacement sensor having a resolution of 1µm. The induced strain S, was measured by dividing the displacement with the thickness of the active layers. It is found to be 0.1% at 650V. **Fig.5** shows the displacement of the actuator with respect to applied voltage. The maximum displacement of 20µm is obtained at 650V.The displacement is approximately linear however the response at low field is relatively small. The inverse piezoelectric coefficient d_{33} in the direction of the applied field can be calculated by using the following relation

$$d_{33}=\delta t/ (nV)$$

Where "8t" is the displacement, "V" is the applied voltage and "n" is the number of the active piezoelectric layers in the actuator. The calculated d_{33} is found to be 1150×10^{-12} m/V at a maximum applied voltage of 650V.

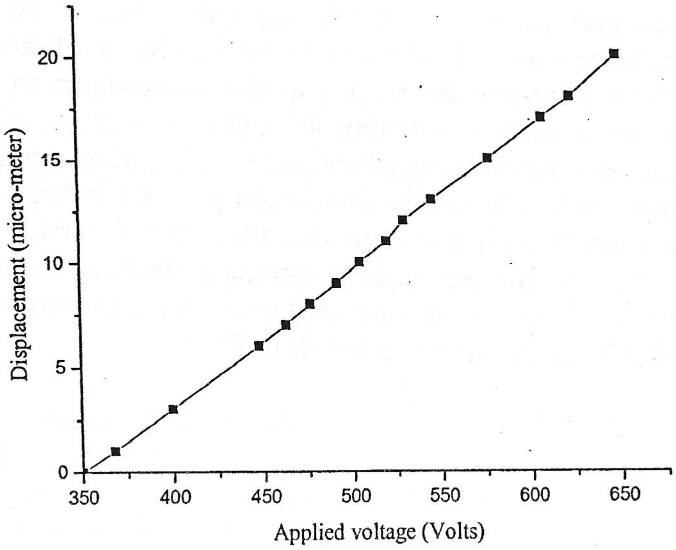

Fig.5. Displacement of a multi-layered stack as the function of applied voltage

Conclusions

Lanthanum, neodymium and strontium doped PZT powders were prepared by wet-chemical method with variation in concentration of the dopants. From the different dopants used 2 mole% Nd^{3+} produces a maximum d_{33} value of 260 pC/N. In case of combined dopants, a combination of 1 mole% Nd^{3+} and 1 mole% Sr^{2+} produced a maximum d_{33} value of 313 pC/N. Few multilayered stacks fabricated from the in house prepared PZT powders produced a maximum displacement of 20µm at 650V. The free strain for the stacks is 0.1% and the inverse piezoelectric coefficient (d_{33}) was 1150 pC/N.

References

1. B. Jaffe, W.R. Cook and H. Jaffe, Piezoelectric Ceramics. , Academic Press, London/New York (1971).
2. K. Kakegawa, J. Mohri, S. Shirasaki and K. Takahasi, J. Am. Ceram. Soc. 65 (1982)515
3. T. Tanaka, Electron. Ceram. Contin. Educ. Sym. 2(1971) 18.
4. S.S. Chandratreya, M.R. Fularth and J.A. Pask, J. Am. Ceram. Soc. 64 (1981) 442.
5. T.R.N. Kutty and R Balachandran, Mater.Res. Bull. 19 (1984) 1479.
6. R.W. Schwartz, D.J. Eichorst and D.A. Payne, Better ceramics through chemistry II, eds. C.J. Brinker, D.E. Clark and D.R. Ulrich (Mater. Res. Soc., Pittsburgh, 1986) 123.
7. Yu- D Tretyakov, M.E. Levina, V.V. Prisedskii, V.A. Fokin and L.G. Gusakova, Inorg. Mater. 13 (1977) 1470.
8. J.V. Biggers and S. Venkataramani, Mater.Res. Bull. 13 (1978) 717.
9. J.F. Fernandez Lozano and C. Mouze, Bol.Soc. Esp. Ceram. Vidue 24 (1977) 769.
10. L. Jong- Kum, L. Kyung Hee and L. Byungtla, Yoop Hakhochi 22(1985) 37.
11. K.D. Budd, S.K. Dey and D.A. Payne, Brit. Ceram. Proc. 36 (1985) 107.
12. L.B.Cong, J.Ma, W.Zhu, and O.K. Tan, Materials letters 52 (2002) 387.